

## APPENDIX A

The methods for resin column preparation, use, and extraction are contained herein as "A Guide to the Preparation and Use of Selected Macroreticular Resins for Environmental Monitoring: North Coast Region" (Fairchild and Klamt, 1986, revised in 1988).



**A GUIDE TO THE  
PREPARATION AND USE OF  
SELECTED MACRORETICULAR RESINS  
FOR ENVIRONMENTAL MONITORING:  
NORTH COAST REGION**

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## INTRODUCTION

Primary funding for this study has been provided by the California State Water Resources Control Board using Section 205(j) grant funds made available by the U.S. Environmental Protection Agency. This does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency or the California State Water Resources Control Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This report is a step-by-step "cookbook" compiled in part from information in reports from the University of California campuses at Santa Cruz (Landing and Bruland 1984) and Davis (Seiber, et.al. 1985) which give more detailed descriptions of the general principles of resin columns as applicable to field sampling. This report is to serve as a guide to the preparation and use of specific resins for environmental monitoring by the North Coast Regional Board under the Water Quality Management Planning Program [Section 205(j)] titled "Toxic Substance Detection and Early Warning for the Russian River".

Resin column monitoring involves the continuous, sampling of water over a specific time period with the accumulation of target chemicals on the resins. Two types of resins are used to monitor dissolved metals and organic compounds:

- 1) Chelating ion exchange resins: These resins accumulate dissolved metals. The metal ions replace existing  $\text{Na}^+$ ,  $\text{NH}_4^+$ , or  $\text{H}^+$  ions in the resin, due to the stronger affinity towards the resin molecules.
- 2) Adsorbent resins: These resins accumulate metal-organic complexes and other organic molecules. The organic molecules are relatively inert with regard to the resins and do not undergo ion exchange, rather are sorbed to the resins. The adsorbent resins vary in polarity, the more polar ones attracting the more polar molecules; adsorbent resins with varying polarities used in series can accumulate a wide variety of molecules.

After being exposed to a water sample the resins must be treated to extract the dissolved metal and/or organic compounds. The extraction techniques differ depending on the compounds being monitored. The resultant extracts are analyzed by atomic absorption spectrometry, high performance liquid chromatography, and/or gas chromatography.

U. C. Santa Cruz (UCSC) reported on the use of resin columns to measure ultra-trace metals in solution and to determine their speciation in fresh waters. Their experiments used an exchange resin to accumulate ions in series with an adsorbent resin to accumulate metal complexes. Four ion exchange resins were studied: CHELEX-100, HQ-8, AG 1-X8, and UCSC HQ-8 (the latter developed by UCSC and not available for commercial use). The adsorbent resin was DUOLITE S-587. Additional information on these resins appears in Appendix A. The resins were characterized with respect to their efficiency and specificity in relation to pH, flow rate through the resins, and the presence of various dissolved organic substances. The resins were packed in Teflon columns and tested for precision and accuracy under field conditions on the Russian and Sacramento Rivers.

U. C. Davis (UCD) reported on the use of resin columns to measure trace organic compounds in water. Since there are many more organic compounds than metals, the UCD report was more complex and analysis was more detailed than in the UCSC report. Amberlite XAD-4 resin was studied and compared in efficiency to liquid-liquid partitioning and polyurethane foam sampling. Chlorinated hydrocarbons, PCBs, and selected esters were studied as special cases in addition to other organic compounds. A survey of the resin column literature is included in the UCD report as well as detailed methodologies for resin extraction and recovery problems. UCD tested the XAD-4 resin for accuracy and precision in Teflon columns with a portable pumping unit on the Russian River, Sacramento Valley streams and agricultural drains, and from a well at Davis.

The major differences in the sampler/pump systems developed at UCD and UCSC were in the pumping direction, column size, pre-filters, and elution/extraction techniques. Though both UCD and UCSC developed automatic accumulative samplers with programmable solenoid valves and a timer to facilitate long-term sampling, only UCSC used this automatic sampler in the field.

UCSC provided positive pressure on the column (i.e. the pump was positioned before the column) while UCD provided suction on the column (i.e. pump was positioned after the column). UCSC used a Flourex cartridge filter as the pre-filter, and UCD used glass wool packed into the resin column separated from the resin by a Teflon screen. The UCSC filter was ahead of the column bank, however the UCD filter preceded each column. Pumping rates for both systems were between 2 and 5 mL per minute.

The total resin column size for the UCSC system was about 5 mL, whereas the UCD system was about 327 mL, about 3/4 of which was glass wool (resin volume of about 40 mL). UCSC performed the elution inside of the columns, whereas UCD removed the resins from the columns for extraction.

Metals recovery tests for Chelex-100 and Duolite S-587 were performed with 500-1000 mL of test spike solution containing organic-free tap water adjusted to pH 6.5 with strong ammonium acetate, a small volume of radiotracer of interest, and 5 mg/L of one of the organic chelators (NTA, EDTA, FA or HA). This solution was passed through the resin columns at various flow rates (2, 5, 8.5 mL/min). Tests were also run at a flow rate of 5 mL/min and various pH's. After passage of the spiked solutions through the resin columns, the resins in the columns were re-suspended with DDIW and placed in 30 mL CPE vials. Radiotracer activities were determined using a Ge(Li) detector. AG 1-X8 was tested in the same manner in the Cl- form using spikes of stable Cr(VI), As(V), and Se(VI) which were added to neutral tap water at ppm levels.

Chelex cation exchange resin quantitatively removed all of the studied metals in the presence of NTA, and FA/HA except for Fe(III) which was recovered on Duolite as anionic FA/HA complexes. At varying pH levels, no more than 20% of the Fe(III) was lost. EDTA held substantial fractions of metal in solution and caused a low collection by the Chelex. However, anionic metal/organic complexes which passed through

the Chelex column were nearly quantitatively retained by the Duolite resin. Using Chelex-100 in series with Duolite S-587 should retain nearly quantitative amounts of dissolved metals in fresh water systems. Flow rates through the resin columns are very important, however since dissociation kinetics will negatively influence the resin collecting efficiency at flow rates above 5 mL/minute.

Organics recovery tests for the XAD-4 resin used a series of pesticides at 10 ug/L and 0.1 ug/L concentrations. At the higher level, recoveries were determined for a number of water samples spiked with mixtures of a few compounds that could be quantitated together using the same analytical techniques. At the lower level, recoveries were determined for water samples spiked with a mixture of compounds from widely differing classes. After compound quantitation using EC and NPD detection with GC columns of varying polarity, this complex mixture was fractionated into compound classes using HPLC. The separate fractions were re-analyzed by GC to determine the extent of clean-up and any effects of fractionation on recoveries (Table 1).

Recoveries averaged  $66.4\% \pm 8.9$  standard deviations (SD) for the 0.1 ug/L level and  $75.6\% \pm 3.1$  SD for the 10 ug/L level. Recovery was better for resin extraction at the lower concentration (0.1 ug/L) than for liquid/liquid solvent extraction. By using both the methylene chloride and acidified acetone extractions in series on a resin bed, most compounds can be quantitatively extracted.

Some compounds required special extraction methods, however. Inter-resin reactions, hydrolysis, volatility, and high dissociation constants necessitate some special techniques for:

- Captan (hydrolysis),
- 1,2-dichloropropane, trichloroethylene, some esters (volatility)
- picloram (inter-resin reactions)
- 2,4-dichlorophenoxyacetic acid, pentachlorophenol (high dissociation constants)
- formaldehyde

Table 1. Recoveries of test compounds from XAD-4 resin for three concentrations in pH 8 tap water as reported by Seiber, et al. (1985).

<u>Compound</u>	Average percent recoveries $\pm$ SD:		
	without HPLC fractionation <u>10 ug/L</u>	<u>0.1 ug/L</u>	with HPLC <u>0.1 ug/L</u>
Pentachlorophenol	85.1 $\pm$ 1.1	72.5 $\pm$ 2.4	---
Tetrachlorophenol	61.4 $\pm$ 1.3	46.7 $\pm$ 4.7	---
Trichlorophenol	74.8 $\pm$ 2.3	77.7 $\pm$ 5.4	---
Aroclor 1232	56.6 $\pm$ 2.3	*	51.4 $\pm$ 4.2
2,8-DCDBF **	---	66.5 $\pm$ 7.8	50.7 $\pm$ 3.9
1,2,3,4-TCDD **	---	53.3 $\pm$ 15.0	38.1 $\pm$ 13.0
2,4-D **	84.7 $\pm$ 1.2	21.5 $\pm$ 4.1	---
Ethion	77.9 $\pm$ 7.3	77.6 $\pm$ 7.2	80.0 $\pm$ 16.3
Diazinon	86.6 $\pm$ 5.6	---	---
Guthion	79.6 $\pm$ 5.0	---	62.6 $\pm$ 12.5
Diuron	64.9 $\pm$ 1.7	*	51.0 $\pm$ 16.4
Atrazine	67.7 $\pm$ 0.2	71.2 $\pm$ 11.9	60.7 $\pm$ 15.7
Amitraz	75.7 $\pm$ 7.4	+	---
Molinate	68.0 $\pm$ 1.1	+	65.0 $\pm$ 14.0

\* 2,8-DCBF = 2,8-dichlorodibenzofuran  
 1,2,3,4-TCDD = 1,2,3,4-tetrachlorodibenzo-p-dioxin  
 2,4-D = 2,4-dichlorophenoxyacetic acid

\*\* background interference

+ co-eluting compounds

++ only one sample analyzed

Table 1. (cont'd).

<u>Compound</u>	Average percent recoveries $\pm$ SD:		
	without HPLC fractionation <u>10 ug/L</u>	<u>0.1 ug/L</u>	with HPLC <u>0.1 ug/L</u>
Endosulfan	76.6 $\pm$ 3.3	70.0 $\pm$ 5.3	65.5 $\pm$ 5.7
Carbaryl	83.3 $\pm$ 2.4	47.3 $\pm$ 11.1	34.8 $\pm$ 3.3
Thiobencarb	90.6 $\pm$ 3.9	81.4 $\pm$ 23.3	95 ++
Captan	1.6 $\pm$ 0.2	---	---
1,2-DCP/TCE **	10.8 $\pm$ 1.2	---	---
Oryzalin	9.4 $\pm$ 1.5	---	---
Picloram	3.9 $\pm$ 0.1	---	---

- \* 2,8-DCBF = 2,8-dichlorodibenzofuran  
 1,2,3,4-TCDD = 1,2,3,4-tetrachlorodibenzo-p-dioxin  
 2,4-D = 2,4-dichlorophenoxyacetic acid  
 \*\* background interference  
 + co-eluting compounds  
 ++ only one sample analyzed

## PART ONE:

### RESIN COLUMN PREPARATION

The importance of clean procedures cannot be over-emphasized. Any introduction of material into the system besides the water to be sampled may cause errant results. The procedures outlined below must be followed without deviation. Log books are essential to proper documentation of procedures and are to be used as identified throughout these procedures. A more comprehensive overall plan for the project quality assurance and control can be found in the document titled "Quality Assurance Program for Toxic Substance Detection and Early Warning For the Russian River".

#### Clean Room Procedures

Ground rules for the use of the clean room involve a basic thought process regarding the introduction of contaminants into the room (Figure 1; See Murphy, 1976 for descriptions of a clean room and Class-100 conditions). All air supplied to the room is, for all practical purposes, 'particulate-free', thus the only way that particles can enter the room is by transport on materials brought into the room. For that reason alone the analyst must always be aware of what is brought into the room. The manner in which one 'dons' and 'ditches' protective clothing is very important to maintaining the clean room environment. Gloves, sleeves, booties, and aprons reduce the amount of particulates that can be transferred from clothing to the clean room environment, and provide some protection to the analyst from acids, etc. as well. The safety glasses are for the technician's protection solely, and must be worn at all times in the clean room. The laminar flow table is the cleanest area of the room, and as such receives the highest degree of attention to reduction of contamination.

1. Turn on HEPA filter system 1 minute prior to entering room
2. Make sure clothes, hair, hand, and face are clean and fairly free from particulates/dust before entering clean room
4. Make sure all necessary items are within clean room (not necessarily under hood, but at least on shelf to be transferred)
3. All protective apparel is stored in the clean room:
  - a. don apron and safety glasses
  - b. don sleeves and gloves before working on laminar flow table (be careful not to transfer material from other areas to the laminar flow table via gloves; if in doubt, put on new gloves)
4. Don't place jars, beakers, etc. on laminar flow table if they have been in contact with "unclean" conditions. For transport put beaker inside another beaker or on 'Precision-wipe' on a clean tray.

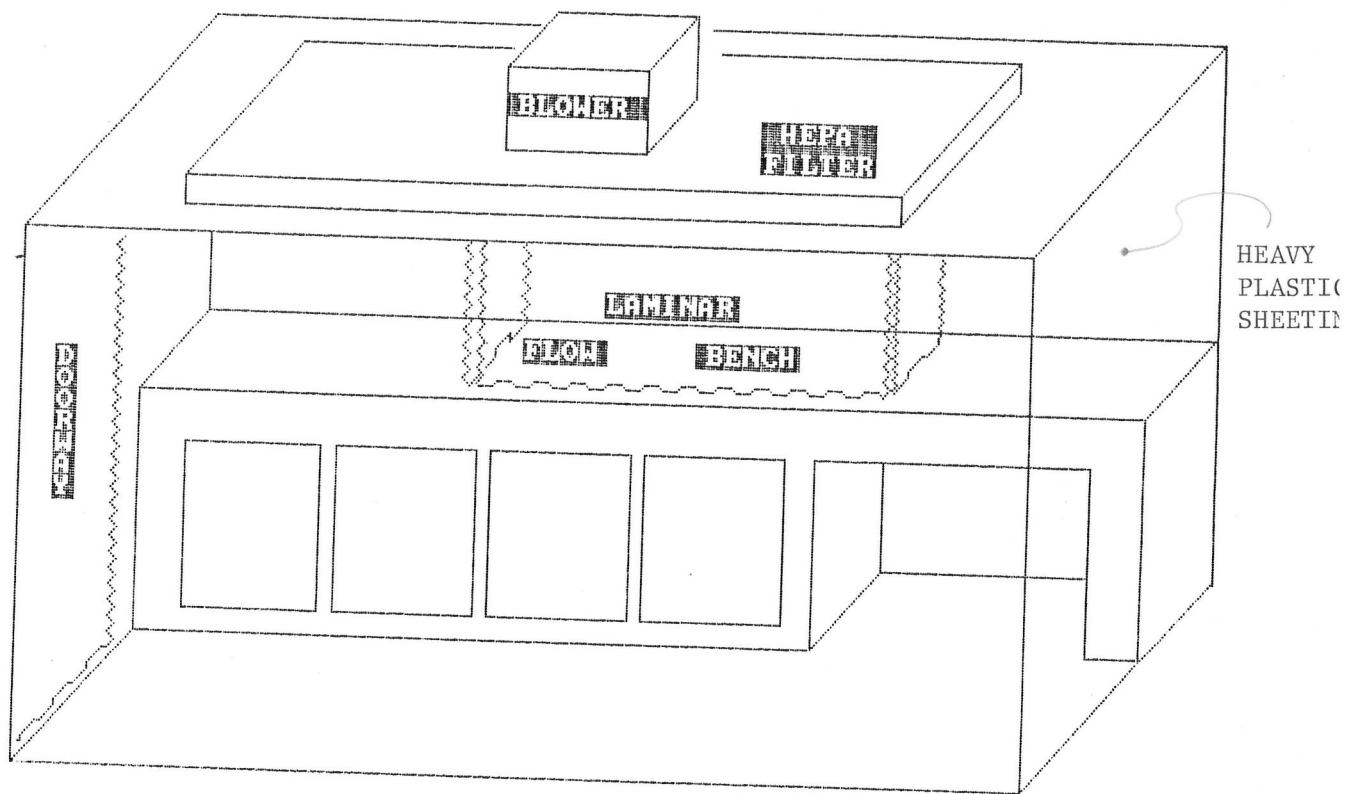


Figure 1. Schematic of clean room constructed in the Sonoma County Water Agency laboratory in Santa Rosa.



5. Don't place head under hood, over laminar flow table
6. Keep note of the prior use of glassware to avoid contamination: water separate from acid separate from ethanol separate from acetone
7. If gloves become contaminated by a spill or touching "unclean" surfaces, throw them away and put on new ones.
8. When leaving wipe down laminar flow table with 1.0 N HNO<sub>3</sub>, followed by DDIW, and "Precision-wipes". Throw away gloves, hang up apron and sleeves, all in reverse of donning.
10. Turn off HEPA filter system after 1 minute.

#### Column cleaning prior to resin packing

The Teflon resin columns are made of 1 cm ID X 1.4 cm OD Teflon tubing. Each end is fitted with Teflon connectors to accomodate 3 mm OD Teflon tubing (Figure 2). The metals and the organics columns are 10 cm long and contain approximately 5 mL ( approx. 5 grams) of resin.

Prior to assembling the resin columns and sampler, batch wash all parts in:

1. acetone (reagent grade quality)
2. dilute micro detergent (Cole-Parmer <sup>TM</sup>)
3. distilled, deionized, organic-free water (DDIW = distilled, deionized water passed through an organics removal resin or activated charcoal)  
(3 rinses),  
(now referred to as Class I cleaned)  
then,
4. soak 24 hrs. in 6.0 M HCl (reagent grade quality)  
(now referred to as Class II cleaned)

cover and store all parts in instra-analyzed (J.T. Baker <sup>TM</sup>) 1.0 N HNO<sub>3</sub> (now referred to as Class III cleaned) in the clean room until use. Label the "batch" and record the date and procedure in the column and resin preparation log book.

#### Metals resins preparation and column packing

All preparation and packing of the columns should be done in the clean room. The following solvents and acids are used in the metals resins preparation and elution, and must be instra-analyzed grade or redistilled with a quartz or Teflon sub-boiling point (sub-B.P.) apparatus:

1. 4.0 M HCl
2. 2.5 N HNO<sub>3</sub>
3. 2.0 M HCl/0.1 N HNO<sub>3</sub> (50:50 solution)



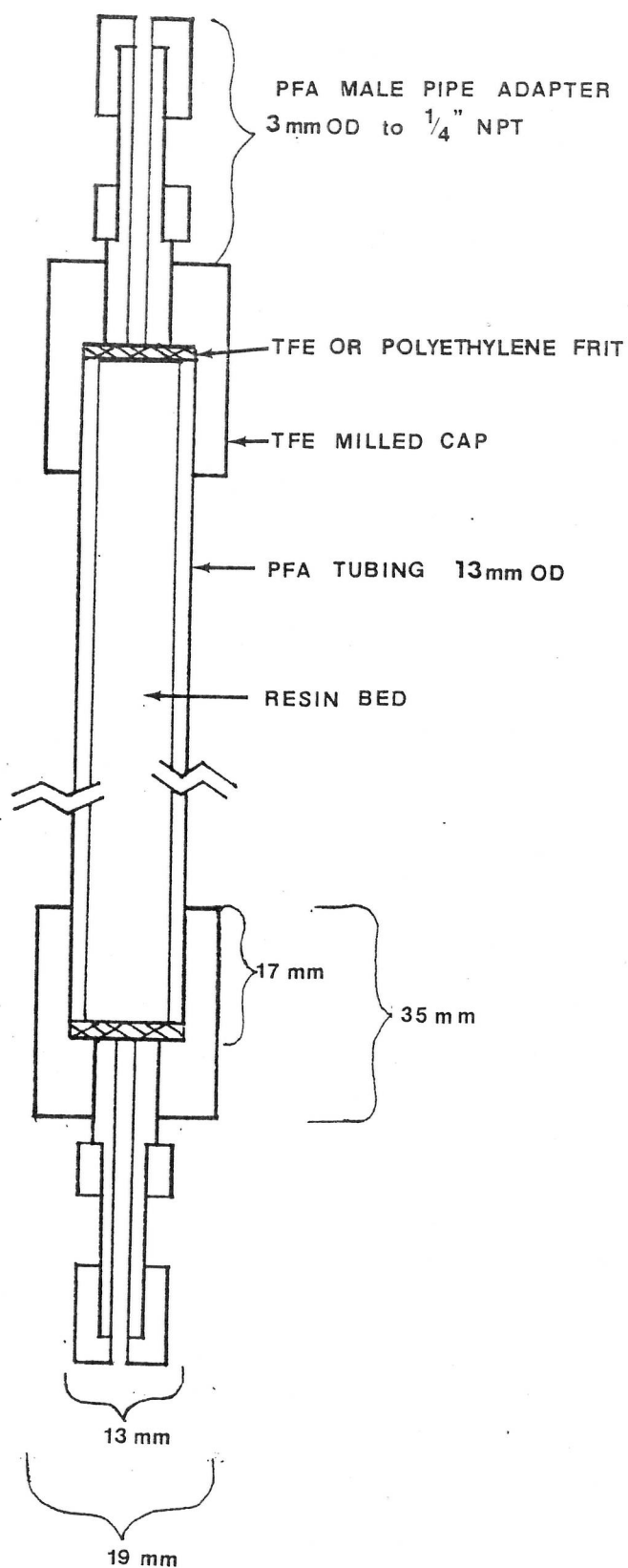


Figure 2. Schematic diagram of Teflon resin column.

4. acetone
6. distilled, deionized, organic-free water (DDIW)
7. 6.0 M HCl
8. 95% ethanol
9. DDIW

Batch clean the resins as follows:

1. DUOLITE S-587, Bio-Rad

Pour 250 ml of 4% (1 M) NaOH over 25 ml of Duolite S-587 in a Class III beaker and allow to soak for 30 min. Decant the base after 30 min. and rinse it three times with approx. 250 ml of DDIW then let soak in 250 ml of DDIW for at least an hour. Rinse the resin until the rinse water is between pH 7 and 10.

2. CHELEX-100, Rohm and Haas

Place 50 ml of resin in the sodium form (as supplied by manufacturer) into a large (diameter = 5 cm) column with a 70 micron Teflon frit on one end. Rinse the resin with 17, 10 mL aliquots of 2.5 N HNO<sub>3</sub> to elute any trace metals. Then rinse the resin slurry with 85 ml of DDIW to remove the excess acid. To convert the resin to the ammonium form, rinse the slurry with 125 ml of 2 N NH<sub>4</sub>OH in 10 ml aliquots. Check the pH of this rinse to insure basicity and complete conversion, then rinse the resin with 125 ml of DDIW to remove excess NH<sub>4</sub>OH.

3. AG 1-X8, Rohm and Haas

AG 1-X8 is used as it arrives from the manufacturer without preparation.



Label prepared resin batches and record all procedures in the column and resin preparation log book.

Prior to resin column packing rinse resins with DDIW until the washes are between pH 7 and 10. Remove the top fitting from a cleaned, DDIW-rinsed Teflon column (see Figure 2) and pour the rinsed resin slurry into the column to a gravity packed volume of approximately 5 mL. Replace the top fitting.





Join the packed columns in appropriate sets (Table 2) with 3 mm OD Teflon tubing. Seal the influent and effluent ends of the column sets by inserting Teflon tubing pieces that were pinched with clean, heated pliers. Double bag the metals columns in polyethylene zip-closure bags that have been rinsed with 1.0 N HNO<sub>3</sub> and allowed to air dry in the clean room, and store in the freezer until use. Label the resin sets and record the resin batch numbers, date of packing, and resin column set number in the log book.

After sampling and extraction, the resins are regenerated with the same procedures as cleaning, with the exception of AG 1-X8, which receives a 50 mL water rinse and 50 mL acid wash with 4.0 M HCl.

Table 2. Resin column configurations for partitioning chemicals, obtaining duplicate samples, and determining resin saturation (breakthrough).

 XAD-4	 XAD-8	 Chelex 100	 AG 1X-8	 Duolite S-587
---	---	---	--	--













### ORGANIC CHEMICALS

	Polar	Non-polar	Both
Routine sampling			 

Duplicates Any of the above sets in parallel

Saturation Above sets in series, like resins grouped  
(i.e., for 'Both' use XAD-4 in series followed by XAD-8)

### METALS

	Ions and labile complexes	As, Cr, Se ions	Both	Complexes only	Ions and complexes
Routine sampling			 		      

Duplicates Any of the above sets in parallel

Saturation Above sets in series, like resins grouped  
(i.e., for 'Both' use Chelex in series followed by AG 1-X8)

## Organics resins preparation and column packing

Although all preparation and packing of the columns will be done by the contract laboratory, Anatec Laboratories, Inc., procedures are outlined below for the reader's information. Two procedures are presented: 1) the first procedure used in preliminary investigations with the XAD-4 resin, and 2) the procedure used in the final testing of the resins. Neither of the methods are necessarily recommended for use, however for those that wish to investigate the use of XAD-4 for environmental monitoring, the second method may be a starting point. The reader is referred to the final 205(j) project report on the resins monitoring results for a more detailed explanation of the investigations leading to the second method (in draft form at this time).

The following solvents are required for the preparation of XAD-4 resin:

1. organic-free distilled water (OFDW - distilled water passed through an organics removal resin or activated charcoal)
2. 0.1 N HCl
3. 0.1 N NaOH
4. methylene chloride
5. ethyl acetate
6. methanol

Place 2 L of the XAD-4 resin in a 4-6 L Pyrex beaker and rinse from the bottom with OFDW to remove silica and small resin particles. Decant the water and wash the resin in turn with:

1. 2 L of 0.1 N HCl (allow to sit 30 minutes)
2. OFDW
3. 2 L of 0.1 N NaOH (allow to sit 30 minutes)
4. OFDW until pH is neutral

Pour the resin slurry into a Soxhlet extractor (2200 mL) containing a fabric sock (Nylon or Dacron) and extract twice each in turn with:

1. methanol for 24 hours,
2. methylene chloride for 24 hours,
3. ethyl acetate for 24 hours,

and extract a final time in methanol for 24 hours and store refrigerated in methanol until used.

Remove the top fitting from a clean, DDIW-rinsed Teflon column, pour the resin slurry into the column to a gravity packed volume of approximately 5 mL, and replace the top fitting.

Wrap the organics columns in foil and store in zip-lock bags. The containerized resin column sets should then be labeled with resin type, date, and technician's name and refrigerated. Record the appropriate information in the log book.

## PART TWO:

### SAMPLING PROCEDURES

#### Sampler description

The automatic sampler/pump system, as designed at UCSC and used by the Regional Board, draws the water through a 3 mm OD (1.5 mm ID) Teflon tube encased in a sheath of flexible polyethylene tubing through an AC peristaltic pump fitted with 25 cm of silicone pump tubing. The sample passes from the pump head to a series of 3-way Teflon solenoid valves controlled by a 4-channel timer/actuator (Figure 3). The valves are actuated (opened) by the timer/actuator and the sample stream passes through a filter cartridge packed with glass wool, then into the resin column set connected to the appropriate valve. The outlet from each resin column set enters a separate collection vessel used to measure the actual volume pumped through each resin column set. In this way, the sampler can run continuously and unattended, collecting subsamples with any of three sets of resin columns over pre-selected time intervals. Several column arrangements are possible and include: (1) a single column, (2) columns in series to determine saturation of the resins and subsequent "break-through", (3) a split stream leading to two parallel sets of columns in series, and (4) sequential columns in series with different resins to partition chemicals by polarity or activity (Table 2).

#### Sampler set-up and dis-connect

If possible, perform the set-up in a clean laboratory, otherwise pick a clean location out of the wind and free from dust. Sampler disconnect can be done in the laboratory, also, but conditions may dictate changing the columns in the field. Have a disposal bag available for gloves, pieces of tubing, etc. and containers for the waste ethanol and acids (1 each). Wear disposable poly gloves during the sampler set-up.

Before connecting the resin column sets to the sampler, join the Teflon exit tubes for each solenoid together at the junctions where each resin column set would be installed (as though the columns were installed).

Rinse the system sequentially with:

1. 300 mL 95% ethanol,
2. at least 600 mL of water to be sampled,

allowing the ethanol to sit in the system for 10 minutes prior to rinsing with the sample water. Collect the ethanol in an appropriately-labeled container; it may be re-distilled for re-use. If the sampler will be moved to sample different waters, then the system should be rinsed with 300 mL 2.0 M HCl/0.1 N HNO<sub>3</sub> (50:50 solution) and 600 mL DDIW after the ethanol.

Be sure to fill the filter cartridge and rinse the entire system with sampling water by activating the various solenoid valves (the controller/actuator is described in the next section). As the water to be sampled is pumped through the system, set the delivery rate of the pump to between two (2) and three (3) mL/minute. This is accomplished by varying the speed setting of the pump motor while measuring the volume delivered for one minute until the desired delivery rate is attained. Check the rate three times to be sure it has stabilized. Record the rate and pump setting in the appropriate resin sampler log book.

Refer to Table 2 for the appropriate resin column combinations prior to attaching the columns to the sampler. The resin column sets are attached as follows:

1. for the metals columns, open ziplocs and remove resin column set, then  
    reseal ziplocs  
    for the organics columns, remove the foil wrapped column from the ziploc  
    and peel the foil back to expose only the input/output tubes
2. remove the pinched ends and store them in a clean jar for use after  
    sampling is completed.
3. attach input/output tubes to the appropriate Teflon sampler tubes.

Be especially careful at all times to minimize contact with the resin columns themselves and any portion of the set up that will contact the sample and/or resin. If field blanks are being used, expose them similarly to the environment, then recap and leave them in the sampler.

Sampler dis-connect is basically the reverse of set-up. Have ready all containers appropriately labeled for the resin column sets. Disconnect the delivery tubes from the resin column sets, drain sample water from column sets into effluent containers (if possible), seal the plastic bags, and place the columns on ice for delivery to the laboratory. After disconnecting the resin column sets, if the sampler is not set-up again immediately, re-join the delivery tubing and rinse the sampler/pump system sequentially with:

1. 300 mL 95% ethanol
  2. 600 mL DDIW
- and if the sampler is to be set-up in a new location, rinse also with:
3. 300 mL 2.0 M HCl/0.1 N HNO<sub>3</sub> (50:50 solution)
  4. 600 mL DDIW,

allowing each solution to sit in the system for 10 minutes. Leave the system filled with DDIW after rinsing, between uses. Collect the ethanol in an appropriately-labeled container; it may be re-distilled for re-use. Collect the waste acid solution in another container for disposal at the laboratory.

## Sampler operation

The controller/actuator can be programmed to open and close the solenoid valves at predetermined intervals and for specific durations. It has a ten (10) program capability, that is, you may program for up to ten different interval/duration combinations. The most common use will be to actuate each valve for a set duration and at even intervals, thus the full 10-program capability would not be used.

Controller use is initiated by first unlocking the keyboard and then entering the time of day.

1. To unlock keyboard: plug in controller and press the buttons 1-0-3-ENTER
2. To enter time: a) press TIME (display will go blank), b) enter time in hours and minutes, c) press AM or PM (red dot to the right of the displaytime indicates PM), d) press ENTER.

CLEAR will remove an incorrect entry, not an entire program. To clear a program, re-type the correct program over it or enter 0 at all stages.

LOCK should be used to lock the keyboard. This will prevent accidental changes in the entered program(s).

The battery pack must be plugged into the back of the controller at this time. In the event of a power loss, the programs will be saved, and automatically resume when power is restored.

Once the time has been entered, the programs may be entered one after the other. Begin programming enough in advance of the ON times to allow the programs to be reviewed for errors. If an error is incurred during any programming sequence, press TIME and start over.

The controller carries the program for the pump variation as well as those for solenoids A, B, and C. The following is a sampling program that has been used to sample on the Russian River. This program allows water to be pumped through three sets of columns for three minutes each, then a thirty minute contact time before more water is pumped. In addition, water is wasted from the pre-filter (Figure 3) for one minute prior to each sampling sequence. This is done to discharge water that has been sitting in the filter since the previous thirty minute sequence and allow new water to be sampled.

### SAMPLE PROGRAM

<u>NUMBER</u>	<u>FUNCTION</u>	<u>ACTIVITY</u>
1	CIRCUIT	FILTER BYPASS
1	ON	(SOL A)
1000AM	VARY	time on
3000+	OFF	repeat every 30 min.
1001AM	VARY	time off
3000+	ENTER	repeat every 30 min.
1	CYCLE	
	ENTER	

# SAMPLE PROGRAM (cont'd.)

<u>NUMBER</u>	<u>FUNCTION</u>	<u>ACTIVITY</u>
2	CIRCUIT	COLUMN SET A
2	ON	(SOL B)
1001AM	VARY	time on
3000+	OFF	repeat every 30 min.
1004AM	VARY	time off
3000+	ENTER	repeat every 30 min.
2	CYCLE	
	ENTER	
3	CIRCUIT	COLUMN SET B
3	ON	(SOL C)
1004AM	VARY	time on
3000+	OFF	repeat every 30 min.
1007AM	VARY	time off
3000+	ENTER	repeat every 30 min.
3	CYCLE	
	ENTER	
4	CIRCUIT	PUMP
4	ON	time on
1001AM	VARY	repeat every 30 min.
3000+	OFF	time off
1010AM	VARY	repeat every 30 min.
3000+	ENTER	
4	CYCLE	
	ENTER	

Note: Water is pumped through column set "C" during the last three minutes of the pump cycle (Figure 3).

Once the controller is programmed, the unit may be secured and left to sample. Periodic checking is suggested to ensure that the sampler is functioning as desired. Record the date and sampling set-up information in the appropriate resin sampler log book.



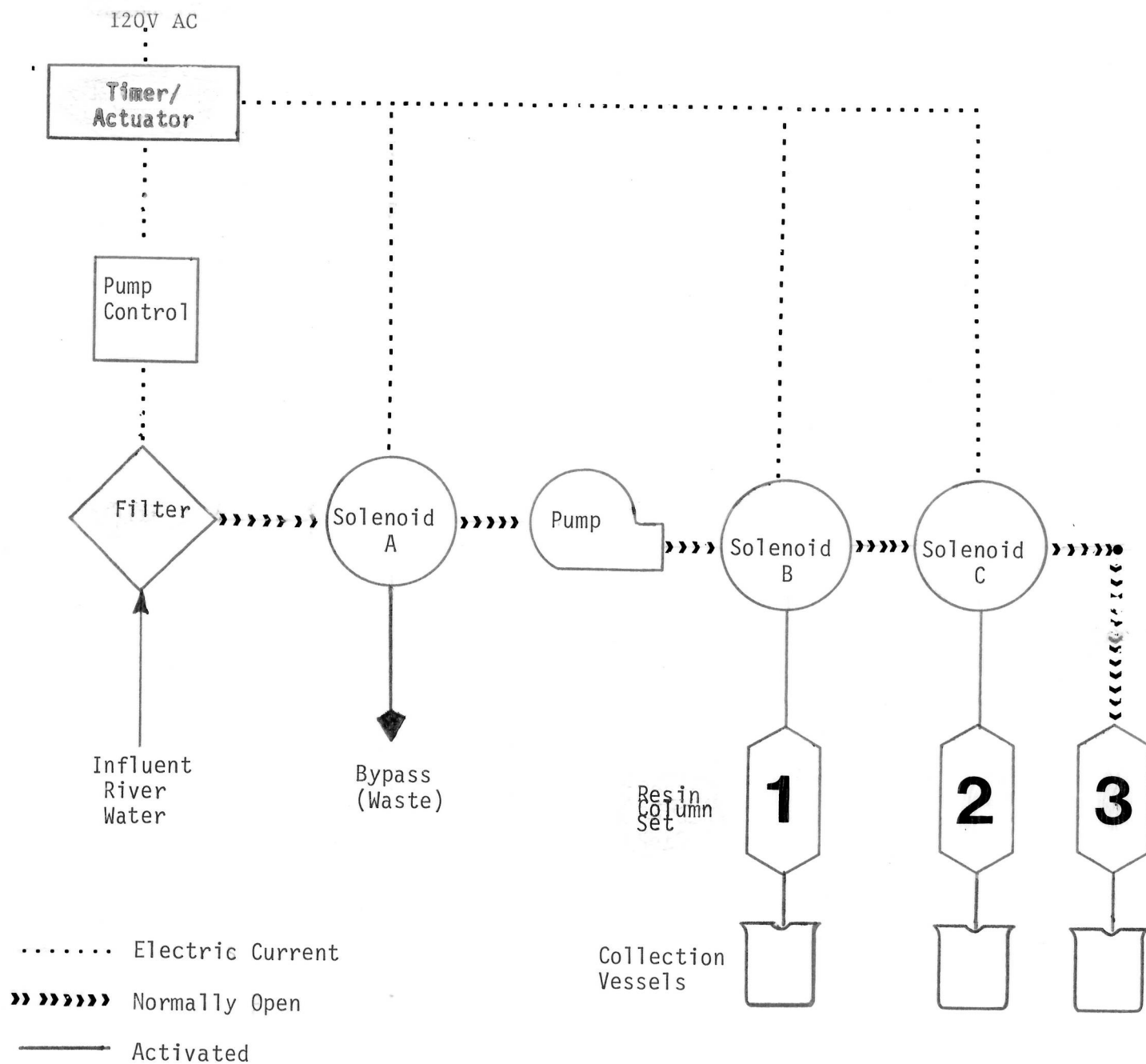


Figure 3. Schematic of the resin column sampler used by the Regional Board.

## PART THREE:

### ELUTION AND ANALYSIS

#### Metals Resins Elution

Elution of all the columns, spiked and blank, should be performed within 24 hrs. of spiking (see Elution Procedures). If columns can not be eluted right after spiking, then refrigerate in Class III zip-lock bags until that time. (For clean room procedures refer to Part One, "Clean Room Procedures", page 7.) Upon arrival at the laboratory, suspend the resin columns upright for 1 hour in the clean room in a single ziplock bag (the outer one removed and discarded outside of the room). After suspension, remove the columns from the ziplock bag and place in a rack on the laminar flow bench. Remove the pinched ends and using a clean, automatic pipetor fitted with a disposable plastic tip, blow air through each column to discharge any residual fluid into a waste beaker. Rinse the pipet tip once with the acid to be used. Place appropriately labeled polyethylene bottles under each column. Do not open the resin columns - elution takes place within the columns, with the exception of AG-1X8. Connect a delivery tube to the bottom end of the resin column and elute the columns with 50 successive 1 mL portions of the appropriate acid. Bring the eluate volume to at least 100 mL. Use the following acids for elution:

1. DUOLITE S-587, use 2.0 M HCl/0.1 N HNO<sub>3</sub>  
After elution, rinse the column with 10 mL DDIW.
2. CHELEX-100, use 2.5 N HNO<sub>3</sub>  
After elution, rinse the column with 10 mL DDIW.
3. AG 1-X8, use 4.0 M HCl, see next paragraph

The AG 1-X8 resin must be degassed prior to elution by rinsing the resin from the column into a Class III beaker with 10.0 mL of 4.0 M HCl. After eight hours or after bubbling stops, rinse the resin and acid slurry back into the column (beneath which has been placed a polyethylene bottle) and elute with 40 successive 1 mL portions of 4.0 M HCl. Bring the volume to at least 100 mL.

Record the eluate volumes and all procedures in the log book. The metals eluates should be delivered to the contract laboratory for analysis.

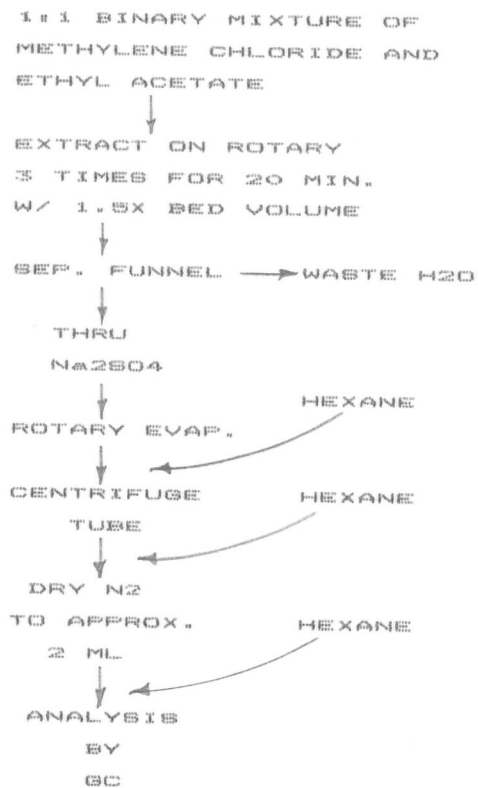
Full contract laboratory quality assurance/quality control procedures require at least 100 mL of eluate for seven analytes, unless mercury is to be analyzed. In the case of mercury, the volume should be increased by 100 mL. The laboratory can analyze for seven metals (with exception of mercury) with a 25-30 mL eluate, however will not be able to perform any quality assurance/quality control checks.

#### Organics Resins Extraction

The resin columns should be delivered to the contract laboratory where the resin will be removed from the column, dried and "salted" with Na<sub>2</sub>SO<sub>4</sub>, and extracted using the appropriate techniques outlined below and diagrammed in Figure 4.

## RESIN EXTRACTIONS - ORGANICS

### NEUTRALS



### ACIDS

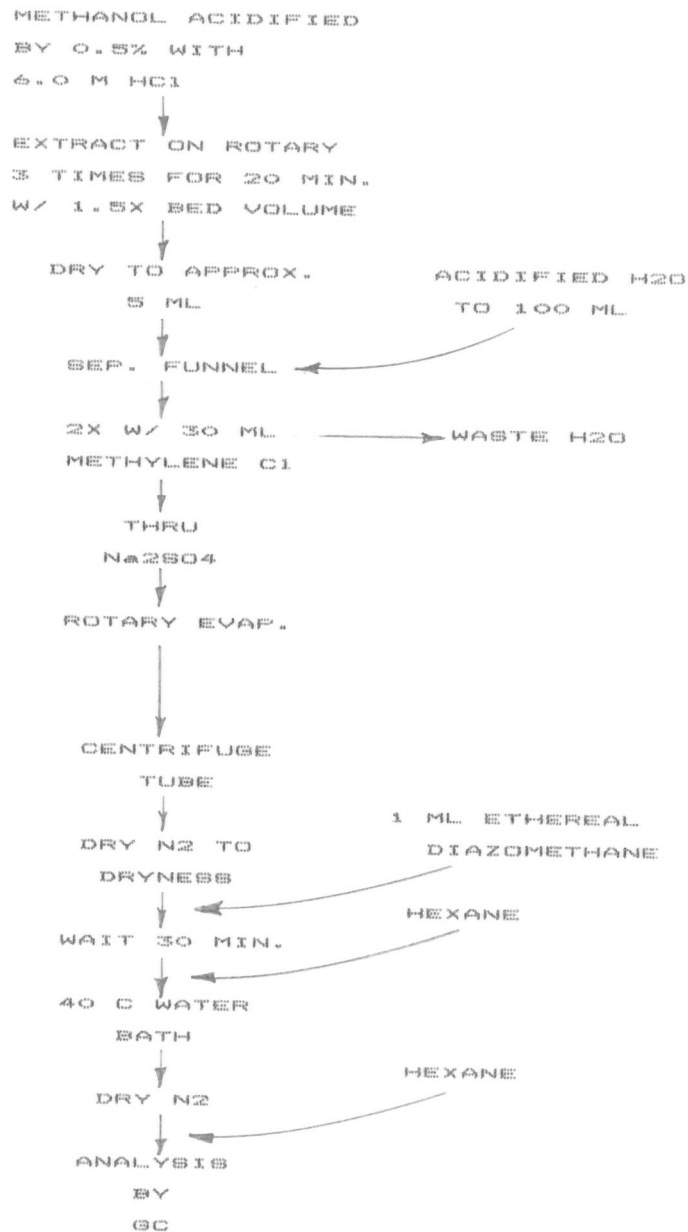


Figure 4. Flow chart of extraction methods used with Amberlite XAD-4 resin.

The original methods as mentioned in Part One, Resin Column Preparation, of this report are presented in Appendix C; the second method used for final experimentation is presented below (and in Appendix C). Neither of the methods are necessarily recommended for use, however for those that wish to investigate the use of XAD-4 for environmental monitoring, the second method may be a starting point. The reader is referred to the final 205(j) project report on the resins monitoring results for a more detailed explanation of the investigations leading to the second method (in draft form at this time).

### Neutral Compounds

Extract the resin three times with a 1:1 binary mixture of methylene chloride and ethyl acetate equivalent to 1.5 times the bed volume (about  $14 \times 1.5 = 21$  mL each time) for 20 minutes each. Pour the combined extracts into a separatory funnel and allow the residual water to separate. The methylene chloride/ethyl acetate layer is then filtered through sodium sulfate into a round-bottom flask, and the extract reduced to 10-15 mL in a rotary evaporator. Nanograde hexane aliquots should be added between concentration steps to remove residual methylene chloride/ethyl acetate. Transfer the extract to a centrifuge tube and further reduce under a stream of dry nitrogen to approximately 2 mL. Replace with hexane for analysis by gas chromatograph.

Acidic compounds and compounds that undergo hydrolysis or with high dissociation constants in water

Extract the resin three times with nanograde methanol acidified to 0.5% (volume-to-volume, v/v) with 6.0 M HCl equivalent to 1.5 times the bed volume (about 21 mL each time). Reduce to approximately 5 mL using a rotary evaporator. Bring the extract to 100 mL with organic-free DW containing 5% (v/v) 6.0 M HCl in a 500 mL separatory funnel. Extract twice with 30 mL aliquots of nanograde methylene chloride (approximately 90 sec. each) using a rotary shaker. Combine the methylene chloride extracts and filter through sodium sulfate into a round-bottom flask. Reduce the extract to 10-15 mL in a rotary evaporator and take it to dryness under a stream of dry nitrogen in a graduated centrifuge tube. Dissolve the residue in about 1 mL of ethereal diazomethane. After 30 minutes dilute the extract with nanograde hexane and place in a 40 C water bath. Remove the excess diazomethane under a stream of dry nitrogen and adjust the extract volume with hexane prior to analysis.

### Organics Analysis Notes

For complex samples where clear resolution of peaks is not possible on gas chromatographic analysis and further separation is needed, fractionation is desirable to separate the sample into sub-samples containing fewer components (Figure 5). Fractionation by HPLC increases detection, but also increases the analysis time and introduces greater product losses. To fractionate by HPLC, use a Particil silica column (10 u, 25 cm X 4.6 mm ID). Inject samples or standard solutions with a mobile phase of 100% hexane at a flow rate of 1 mL/minute. Begin a linear gradient immediately after injection, from 100% hexane to 100%

methyl t-butyl ether (MTBE) over a 30 minute period. Hold the mobile phase composition at 100% MTBE for 15 minutes, then recycle the system to 100% hexane and allow to re-equilibrate for 30 minutes prior to the next injection. Collect fractions manually in 15 mL centrifuge tubes at timed intervals of three minute multiples. Fractions 1 through 3 are each sequentially collected for about 9 minutes (9 mL) starting 3 minutes after injection (holdup time). Fraction 4 is collected for 15 minutes to complete the gradient. Concentrate each fraction under nitrogen as necessary prior to analysis by gas chromatograph.

If fractionation by HPLC is not the chosen route, analyze by gas chromatograph using the appropriate cleanup techniques and columns and detectors for the compounds desired.



## REFERENCES CITED

- Landing, W.M. and K.W. Bruland. 1985. The Design and Use of a Flow-through, Time-integrating, Concentrating/sampling System for the Determination of Trace Element Concentrations and Speciation in Fresh Waters. Draft report for State of Calif., Water Resources Control Bd. Contract No. 2-121-420-0: 48 pp.
- Murphy, T.J. 1976. The Role of the Analytical Blank in Accurate Trace Analysis in Nat. Bureau of Standards. 1976. Accuracy in Trace Analysis. Spec. Pub. 422: 509-539.
- Seiber, J.N., T.L. Shibamoto, M. Majewski, C. Reece, and J.E. Woodrow. 1985. Development and Testing of Resin Column Method for Accumulative Sampling of Trace Organics in River Water. Draft report for State of Calif., Water Resources Control Bd. Contract No. 2-123-428-0: 138 pp.

## APPENDIX A

### SUPPLIES- METALS

#### A. Resins

1. AG 1-X8 anion exchange resin for detection of oxyanionics
  - a. 100-200 mesh; Bio-Rad
  - b. minimum wet capacity = 1.2 meq/mL
  - c. typical ion exchange -  $\text{Cr(4)O}_4^{--}$  displaces 2  $\text{Cl}^-$  ions.
2. Chelex-100 cation exchange - styrene divinyl benzene polymer
  - a. 100-200 mesh; Bio-Rad
  - b. minimum wet capacity = 0.4 meq/mL
  - c. typical exchange -  $\text{Cu}^{++}$  displaces 2  $\text{Na}^+$ ,  $\text{NH}_4^+$ , or  $\text{H}^+$
3. Duolite S-587 adsorbent - phenolic formaldehyde polymer with amino functional groups.
  - a. 16-50 mesh; Diamond, Shamrock/Rohm & Haas
  - b. has some ion exchange capability ( $\text{Cl}^-$  exchange).
4. UCSC HQ-8 cation exchange resin-8-hydroxyquinoline, silica immobilized (not available commercially)
5. HQ-8 cation exchange resin, 8-hydroxyquinoline, polystyrene divinyl benzene immobilized
  - a. 20-50 mesh; Sea-Chem

#### B. Solvents (redistilled w/ a quartz sub-B.P. apparatus or Instralyzed, J.T. Baker <sup>TM</sup>)

1. 4 M HCl
2. 2.5 N  $\text{HNO}_3$
3. 2.0 M HCl/0.1 N  $\text{HNO}_3$
4. Acetone
5. Dilute micro detergent (Cole-Parmer)
6. Quartz distilled, deionized water
7. 6.0 M HCl
8. 95% ethanol
9. Organic-free water (pH 6.5)

### SUPPLIES- ORGANICS

#### A. Resins

1. Amberlite XAD-4 polystyrenedivinylbenzene co-polymer also XAD-7 & 8 (more polar, mentioned in UCD report)
  - a. 20-60 mesh; Rohm & Haas
  - b. surface area =  $725 \text{ M}^2/\text{g}$ ; ave. pore diameter = 40 Angstroms
2. Polyurethane Foam-Type A - collects PCBs
3. HPLC reverse phase packing materials

#### B. Solvents

1. Methylene Chloride



B. Solvents (cont'd)

2. Methanol
3. Hexane-HPLC grade
4. Methyl t-butyl ether - HPLC grade
5. Diazomethane (N-methyl-N-nitroso-p-toluenesulfonamide)
6. Diethyl ether
7. Acetone
8. 0.1 M NaOH
9. 0.1 M HCl

## APPENDIX B

### UCSC REPORT - METALS

- Samples taken on the Russian River, Sacramento River, Merced River.
- Results are discussed on pg.23-33 with data tables beginning at Table 5.
- The report from June 1985 did not include description of field sampling.

### UCD REPORT - ORGANICS

- Russian River at Cooks Beach, Wohler Dam, and Turula Prop.  
(pp.66 & 70-88)
  1. Samples taken over 12 hour, 24 hour, and 5 day periods.
  2. Samples frozen on dry ice until analysis.
  3. Analysis by fractionation & GC
    - a.Extraction done for neutral and acidic fractions (see Figs. III-B and III-C, respectively)
    - b.Neutral samples showed no significant peaks above background
    - c.Acidity sample contained DDT at 2.25ppb, DDE at 0.21ppb, DDD at 0.013ppb(pg.74-75). Another sample showed PCP levels above background.
    - d.Results confirmed w/GC and/or mass spectroscopy.
- Sacramento Valley Drains sampled at R.D.-108 & Fremont Weir  
(pp.67 & 88-90)
- Municipal Well at Davis - tested for ethylene dibromide (p.68 & 90-91)
  1. Samples taken over 7 hour period.
  2. Increased resin charge to 80 mL wet resin due to increased flow rate.
- Conclusions
  1. Low detection levels (sub-ppb) are attained after fractionating neutral (methylene chloride) and acidic (acetone/HCl) extracts separately.
  2. XAD resin was slightly less efficient than solvent extraction.
  3. Problems with formaldehyde extraction and solvent breakthrough.
  4. For formaldehyde extraction see Analytical Chem. - JAN.'85

Teflon fittings	filter holder, PFA, 1/4" OD ferrules (Cole-Parmer # TV-6621-40)  straight union reducer, 1/4" OD to 1/8" OD (Cole-Parmer # TV-6373-71)  male pipe adapter, TFE, 1/8" NPT to 1/8" tubing, with knurled nut (Berghof # TMP-S022-F(K))
Teflon rod	TFE, 3/4"  Cadillac Plastics 650 Dubuque Street South San Francisco, CA 94080
Resins	Chelex-100, 100-200 mesh, sodium form AG 1X-8, 100-200 mesh, chloride form  Bio-Rad Laboratories P.O. Box 4031 Richmond, CA 94804  Duolite S-587  Rohm and Haas Company Philadelphia, PA 19105

## APPENDIX B

### Resin Sampler Parts List

The names of manufacturers and trade names are given as a guide to availability of the supplies and in no way should be construed as a recommendation or endorsement.

Timer/actuator	Lindburg Enterprises, Inc. 9707 Candida Street San Diego, CA 92126  Chrontrol R Model CD-4, 110 volt AC Chrontrol R Model CD-4S, 12 volt DC
Solenoid valves	1/8" orifice, 1/8" female NPT, 3-way  DC-operated model DV3-122 Fluorocarbon 1754 S. Clementine Anaheim, CA 92803  AC-operated model # SF22A53W Berghof/America, Inc. Main Street Raymond, NH 03077
Pump	Masterflex R peristaltic, variable speed (1-100 RPM)  DC-operated model # 7533-20 AC-operated model # 7553-10  pump head model # 701420  Cole-Parmer Instrument Co. 7425 N. Oak Park Avenue Chicago, IL 60648
Tubing	Teflon, PFA, 1/2" OD, 1/16" wall thickness Teflon, PFA, TFE, or FEP, 1/8" OD heavy-walled



## APPENDIX C

### Organics preparation and extraction methods.

Two methods are presented herein: 1) the first procedure used in preliminary investigations with the XAD-4 resin, and 2) the procedure used in the final testing of the resins. Neither of the methods are necessarily recommended for use, however for those that wish to investigate the use of XAD-4 for environmental monitoring, the second method may be a starting point. The reader is referred to the final 205(j) project report on the resins monitoring results for a more detailed explanation of the investigations leading to the second method (in draft form at this time).

#### Method 1

##### Resin preparation

The following solvents are required in the preparation of XAD resins by this method:

1. organic-free distilled water (OFDW - distilled water passed through an organics removal resin or activated charcoal)
2. 0.1 N NaOH
3. re-distilled drum acetone
4. methylene chloride
5. methanol

Place 2 L of the XAD-4 resin in a 4-6 L Pyrex beaker and rinse from the bottom with OFDW to remove silica and small resin particles. Decant the water and wash the resin in turn with:

1. 2 L of 0.1 N NaOH (allow to sit 30 minutes)
2. OFDW
3. 2 L of 0.1 M HCl (allow to sit 30 minutes)
4. OFDW
5. 2 L of redistilled drum acetone, three times

Pour the resin slurry into a Soxhlet extractor (2200 mL) containing a fabric sock (Nylon or Dacron) and extract in turn with:

1. acetone for 24 hours,
2. methylene chloride for 24 hours,
3. methanol for 24 hours,

and store in methanol under refrigeration until used.

Remove the top fitting from a clean, DDIW-rinsed Teflon column, pour the resin slurry into the column to a gravity packed volume of approximately 5 mL, and replace the top fitting.

Wrap the organics columns in foil and store in zip-lock bags. The containerized resin column sets should then be labeled with resin type, date, and technician's name and refrigerated. Record the appropriate information in the log book.

## Resin extraction

### Methylene Chloride Extraction (for neutral compounds)

Extract the resin three times with nanograde methylene chloride equivalent to 1.5 times the bed volume (about  $14 \times 1.5 = 21$  mL each time) for 20 minutes each. Pour the combined extracts into a separatory funnel and allow the residual water to separate. The methylene chloride layer is then filtered through sodium sulfate into a round-bottom flask, and the extract reduced to 10-15 mL in a rotary evaporator. Nanograde hexane aliquots should be added between concentration steps to remove residual methylene chloride. Transfer the extract to a centrifuge tube and further reduce under a stream of dry nitrogen. Replace with hexane for analysis by gas chromatograph.

### Acetone Extraction (for acidic compounds and compounds that undergo hydrolysis or with high dissociation constants in water)

Extract the resin three times with nanograde acetone acidified to 5% (volume-to-volume, v/v) with 6.0 M HCl equivalent to 1.5 times the bed volume (about 21 mL each time). Reduce to 10-15 mL, if necessary, using a rotary evaporator. Combine the 10-15 mL extract with 100 mL DW containing 5% (v/v) 6.0 M HCl in a 500 mL separatory funnel. Extract twice with 30 mL aliquots of methylene chloride (approximately 90 sec. each) using a rotary shaker. Combine the methylene chloride extracts and filter through sodium sulfate into a round-bottom flask. Reduce the extract to 10-15 mL in a rotary evaporator and take it to dryness under a stream of dry nitrogen in a graduated centrifuge tube. Dissolve the residue in about 1 mL of ethereal diazomethane. After 30 minutes dilute the extract with nanograde hexane and place in a 40 C water bath. Remove the excess diazomethane under a stream of dry nitrogen and adjust the extract volume with hexane prior to analysis.

### Diethyl ether extraction (for ethylene dibromide)

Extract three times with nanograde diethyl ether equivalent to 1.5 times the bed volume (about 21 mL each time). Reduce in a 500 mL Kuderna-Danish (K-D) evaporating flask fitted with a 3-ball Snyder column and a 10 mL concentrator tube. If excess water is present in the system, dilute with 25 mL DW and extract again in a separatory funnel three times with 15 mL aliquots of nanograde hexane. Dry the extracts over sodium sulfate, combine, and reduce in volume using a 250 mL K-D flask.

## Method 2

### Resin preparation

The following solvents are required in the preparation of XAD resins by this method:

1. organic-free distilled water (OFDW - distilled water passed through an organics removal resin or activated charcoal)
2. 0.1 N HCl
3. 0.1 N NaOH
4. methylene chloride
5. ethyl acetate
6. methanol

Place 2 L of the XAD-4 resin in a 4-6 L Pyrex beaker and rinse from the bottom with OFDW to remove silica and small resin particles. Decant the water and wash the resin in turn with:

1. 2 L of 0.1 M HCl (allow to sit 30 minutes)
2. OFDW
3. 2 L of 0.1 N NaOH (allow to sit 30 minutes)
4. OFDW until pH is neutral

Pour the resin slurry into a Soxhlet extractor (2200 mL) containing a fabric sock (Nylon or Dacron) and extract in turn with:

1. methanol for 24 hours,
2. methylene chloride for 24 hours,
3. ethyl acetate for 24 hours,

and extract a final time in methanol for 24 hours and store refrigerated in methanol until used.

Remove the top fitting from a clean, DDIW-rinsed Teflon column, pour the resin slurry into the column to a gravity packed volume of approximately 5 mL, and replace the top fitting.

Wrap the organics columns in foil and store in zip-lock bags. The containerized resin column sets should then be labeled with resin type, date, and technician's name and refrigerated. Record the appropriate information in the log book.



## Resin extraction

### Neutral Compounds

Extract the resin three times with a 1:1 binary mixture of methylene chloride and ethyl acetate equivalent to 1.5 times the bed volume (about  $14 \times 1.5 = 21$  mL each time) for 20 minutes each. Pour the combined extracts into a separatory funnel and allow the residual water to separate. The methylene chloride/ethyl acetate layer is then filtered through sodium sulfate into a round-bottom flask, and the extract reduced to 10-15 mL in a rotary evaporator. Nanograde hexane aliquots should be added between concentration steps to remove residual methylene chloride/ethyl acetate. Transfer the extract to a centrifuge tube and further reduce under a stream of dry nitrogen to approximately 2 mL. Replace with hexane for analysis by gas chromatograph.

Acidic compounds and compounds that undergo hydrolysis or with high dissociation constants in water

Extract the resin three times with nanograde methanol acidified to 0.5% (volume-to-volume, v/v) with 6.0 M HCl equivalent to 1.5 times the bed volume (about 21 mL each time). Reduce to approximately 5 mL using a rotary evaporator. Bring the extract to 100 mL with organic-free DW containing 0.5% (v/v) 6.0 M HCl in a 500 mL separatory funnel. Extract twice with 30 mL aliquots of nanograde methylene chloride (approximately 90 sec. each) using a rotary shaker. Combine the methylene chloride extracts and filter through sodium sulfate into a round-bottom flask. Reduce the extract to 10-15 mL in a rotary evaporator and take it to dryness under a stream of dry nitrogen in a graduated centrifuge tube. Dissolve the residue in about 1 mL of ethereal diazomethane. After 30 minutes dilute the extract with nanograde hexane and place in a 40 C water bath. Remove the excess diazomethane under a stream of dry nitrogen and adjust the extract volume with hexane prior to analysis.

